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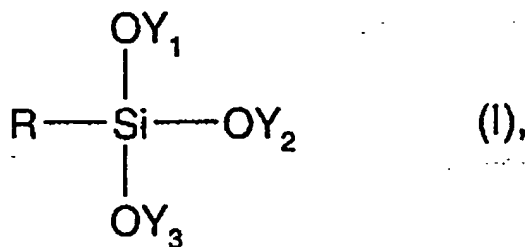
(71) CIBA SPECIALTY CHEMICALS HOLDING INC., CH

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(54) **ADHESIF A BASE DE CYCLOOLEFINE**

(54) **CYCLOOLEFIN-BASED ADHESIVE**



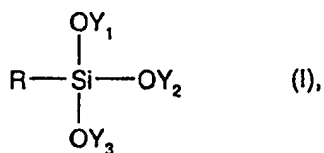
(57) La présente invention porte sur l'emploi, comme adhésif, d'une composition renfermant (a) au moins une cyclooléfine, (b) un catalyseur pour la polymérisation par métathèse avec ouverture de cycle, (c) une charge, (d) un silane de formule I (voir formule I), où R est un groupe organique monovalent de 2 à 100 atomes de carbone, dont un ou plusieurs peuvent être remplacés par des atomes d'oxygène, de soufre, d'azote ou de silicium, et où Y<sub>1</sub>, Y<sub>2</sub> et Y<sub>3</sub> sont chacun indépendamment l'un de l'autre un groupe alkyle C<sub>1</sub>-C<sub>20</sub>, aryle C<sub>5</sub>-C<sub>20</sub>, aralkyle C<sub>6</sub>-C<sub>20</sub>, cycloalkyle C<sub>5</sub>-C<sub>12</sub>, alcoxyalkyle C<sub>2</sub>-C<sub>20</sub> ou acyle C<sub>1</sub>-C<sub>20</sub>.

(57) The invention relates to the use, as an adhesive, of a composition comprising (a) at least one strained cycloolefin, (b) a catalyst for ring-opening metathesis polymerisation, (c) a filler and (d) a silane of formula I (see formula I), wherein R is a monovalent organic group having from 2 to 100 carbon atoms, one or more of which may have been replaced by oxygen, sulfur, nitrogen or silicon atoms, and Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>5</sub>-C<sub>20</sub>aryl, C<sub>6</sub>-C<sub>20</sub>aralkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, C<sub>2</sub>-C<sub>20</sub>alkoxyalkyl or C<sub>1</sub>-C<sub>20</sub>acyl.

Abstract of the Disclosure

The invention relates to the use, as an adhesive, of a composition comprising

- (a) at least one strained cycloolefin,
- (b) a catalyst for ring-opening metathesis polymerisation,
- (c) a filler and
- (d) a silane of formula I



wherein R is a monovalent organic group having from 2 to 100 carbon atoms, one or more of which may have been replaced by oxygen, sulfur, nitrogen or silicon atoms, and Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>5</sub>-C<sub>20</sub>aryl, C<sub>6</sub>-C<sub>20</sub>aralkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, C<sub>2</sub>-C<sub>20</sub>alkoxyalkyl or C<sub>1</sub>-C<sub>20</sub>acyl.

Cycloolefin-based adhesive

The present invention relates to the use, as an adhesive, of a composition comprising a strained cycloolefin, a catalyst, a filler and a silane, and to a method of bonding substrates.

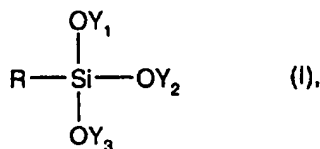
In WO 96/16100 and WO 96/20235 it is mentioned that the ROMP systems (ROMP = ring-opening metathesis polymerisation) described therein based on strained cycloolefins and specific ruthenium catalysts are suitable as adhesives for bonding Teflon, polyethylene and polypropylene. The adhesion to the substrate is inadequate for certain uses, however, owing to the low polarity of the cycloolefins.

Bonds made with reactive adhesives exhibit inner strains caused by reaction shrinkage when the relatively large intermolecular spacing between the monomers are replaced by the closer spacing of the covalent bonds between the polymer segments. The shrinkage can be reduced by the addition of suitable fillers, but the addition of fillers generally results in a breakdown of the cohesion.

Surprisingly, it has now been found that the ROMP systems described in EP-A-771 830, together with fillers, exhibit very good adhesion and can consequently be used as adhesives.

The present invention relates to the use, as an adhesive, of a composition comprising

- (a) at least one strained cycloolefin,
- (b) a catalyst for ring-opening metathesis polymerisation,
- (c) a filler and
- (d) a silane of formula I



wherein R is a monovalent organic group having from 2 to 100 carbon atoms, one or more of which may be replaced by oxygen, sulfur, nitrogen or silicon atoms, and Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>5</sub>-C<sub>20</sub>aryl, C<sub>6</sub>-C<sub>20</sub>aralkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, C<sub>2</sub>-C<sub>20</sub>alkoxyalkyl or C<sub>1</sub>-C<sub>20</sub>acyl.

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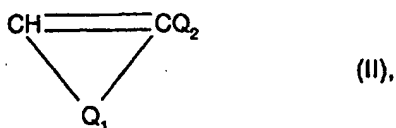
When fully cured, the ROMP system exhibits an especially high degree of adhesion to metals, for example iron or aluminium. Preference is accordingly given to the use of the above-specified composition as an adhesive for metals, especially for aluminium.

Within the scope of the present invention there is to be understood by "strained cycloolefin" any cycloolefin, with the exception of cyclohexene and derivatives thereof, which cannot be polymerised by ring-opening metathesis.

Strained cycloolefins may be monocyclic or polycyclic fused or bridged ring systems, for example having from two to four rings, that are unsubstituted or substituted and may contain hetero atoms, for example oxygen, sulfur, nitrogen or silicon, in one or more rings and/or may contain fused aromatic or heteroaromatic rings, for example o-phenylene, o-naphthylene, o-pyridinylene or o-pyrimidinylene. The individual cyclic rings may contain from 3 to 16, especially from 3 to 12, and more especially from 3 to 8, ring members. The strained cycloolefins may contain further non-aromatic double bonds, preference being given, depending on the ring size, to from 2 to 4 such additional double bonds. The ring substituents are inert, that is to say those substituents do not impair the chemical stability and the thermostability of the ROMP catalysts.

When the strained cycloolefins contain more than one double bond, for example from 2 to 4 double bonds, it is possible also for crosslinked polymers to be formed, depending on the reaction conditions, the monomer selected and the amount of catalyst.

There is preferably used as component (a) in the composition according to the invention a compound of formula II



wherein  $Q_1$  is a radical having at least one carbon atom, which radical, together with the  $-CH=CQ_2$  group, forms an alicyclic ring having a minimum of three members that may contain one or more hetero atoms selected from the group silicon, phosphorus, oxygen, nitrogen and sulfur and that is unsubstituted or substituted by halogen,  $=O$ ,  $-CN$ ,  $-NO_2$ ;  $R_1R_2R_3Si-(O)_n$ ,  $-COOM$ ,  $-SO_3M$ ,  $-PO_3M$ ,  $-COO(M_1)_{1/2}$ ,  $-SO_3(M_1)_{1/2}$ ,  $-PO_3(M_1)_{1/2}$ ,  $C_1-C_{20}alkyl$ ,  $C_1-C_{20}hydroxyalkyl$ ,  $C_1-C_{20}haloalkyl$ ,  $C_1-C_6cyanoalkyl$ ,  $C_3-C_8cycloalkyl$ ,  $C_6-C_{16}aryl$ ,  $C_7-C_{16}$

aralkyl, C<sub>3</sub>-C<sub>6</sub>heterocycloalkyl, C<sub>3</sub>-C<sub>16</sub>heteroaryl, C<sub>4</sub>-C<sub>16</sub>heteroaralkyl or by R<sub>4</sub>-X-; or in which two adjacent carbon atoms are bonded by -CO-O-CO- or -CO-NR<sub>5</sub>-CO-; or in which there is fused to adjacent carbon atoms of the alicyclic ring an alicyclic, aromatic or heteroaromatic ring that is unsubstituted or substituted by halogen, -CN, -NO<sub>2</sub>, R<sub>6</sub>R<sub>7</sub>R<sub>8</sub>Si-(O)<sub>u</sub>-, -COOM, -SO<sub>3</sub>M, -PO<sub>3</sub>M, -COO(M<sub>1</sub>)<sub>1/2</sub>, -SO<sub>3</sub>(M<sub>1</sub>)<sub>1/2</sub>, -PO<sub>3</sub>(M<sub>1</sub>)<sub>1/2</sub>, C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>1</sub>-C<sub>20</sub>haloalkyl, C<sub>1</sub>-C<sub>20</sub>hydroxyalkyl, C<sub>1</sub>-C<sub>6</sub>cyanoalkyl, C<sub>3</sub>-C<sub>8</sub>cycloalkyl, C<sub>6</sub>-C<sub>16</sub>aryl, C<sub>7</sub>-C<sub>16</sub>aralkyl, C<sub>3</sub>-C<sub>6</sub>heterocycloalkyl, C<sub>3</sub>-C<sub>16</sub>heteroaryl, C<sub>4</sub>-C<sub>16</sub>heteroaralkyl or by R<sub>13</sub>-X<sub>1</sub>-; X and X<sub>1</sub> are each independently of the other -O-, -S-, -CO-, -SO-, -SO<sub>2</sub>-, -O-CO-, -COO-, -CO-NR<sub>5</sub>-, -NR<sub>10</sub>-CO-, -SO<sub>2</sub>-O- or -O-SO<sub>2</sub>-; R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are each independently of the other C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>perfluoroalkyl, phenyl or benzyl; R<sub>4</sub> and R<sub>13</sub> are each independently of the other C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>1</sub>-C<sub>20</sub>haloalkyl, C<sub>1</sub>-C<sub>20</sub>hydroxyalkyl, C<sub>3</sub>-C<sub>8</sub>cycloalkyl, C<sub>6</sub>-C<sub>16</sub>aryl or C<sub>7</sub>-C<sub>16</sub>aralkyl; R<sub>5</sub> and R<sub>10</sub> are each independently of the other hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl or benzyl, the alkyl groups in turn being unsubstituted or substituted by C<sub>1</sub>-C<sub>12</sub>alkoxy or by C<sub>3</sub>-C<sub>8</sub>cycloalkyl; R<sub>6</sub>, R<sub>7</sub> and R<sub>8</sub> are each independently of the others C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>perfluoroalkyl, phenyl or benzyl; M is an alkali metal and M<sub>1</sub> is an alkaline earth metal; and u is 0 or 1; it being possible for the alicyclic ring formed with Q<sub>1</sub> to contain further non-aromatic double bonds; Q<sub>2</sub> is hydrogen, C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>1</sub>-C<sub>20</sub>haloalkyl, C<sub>1</sub>-C<sub>12</sub>alkoxy, halogen, -CN or R<sub>11</sub>-X<sub>2</sub>-; R<sub>11</sub> is C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>1</sub>-C<sub>20</sub>haloalkyl, C<sub>1</sub>-C<sub>20</sub>hydroxyalkyl, C<sub>3</sub>-C<sub>8</sub>cycloalkyl, C<sub>6</sub>-C<sub>16</sub>aryl or C<sub>7</sub>-C<sub>16</sub>aralkyl; X<sub>2</sub> is -COO- or -CO-NR<sub>12</sub>-; and R<sub>12</sub> is hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl or benzyl; wherein the above-mentioned cycloalkyl, heterocycloalkyl, aryl, heteroaryl, aralkyl and heteroaralkyl groups may be unsubstituted or substituted by C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>1</sub>-C<sub>12</sub>alkoxy, -NO<sub>2</sub>, -CN or by halogen, and wherein the hetero atoms of the above-mentioned heterocycloalkyl, heteroaryl and heteroaralkyl groups are selected from the group -O-, -S-, -NR<sub>9</sub>- and -N=, R<sub>9</sub> being hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl, phenyl or benzyl.

Fused-on alicyclic rings contain preferably from 3 to 8, especially from 4 to 7, and more especially 5 or 6, ring carbon atoms.

For the purpose of crosslinking or to control the molecular weight, the composition according to the invention may contain further olefins capable of metathesis, advantageously in amounts of up to 40 mol %, especially from 0.01 to 30 mol % and more especially from 0.1 to 20 mol %, based on the total amount of the cycloolefins and olefins present.

Suitable olefins capable of metathesis are, for example, cyclooctadiene, cyclooctatriene, norbornadiene and acetylnorbornene. Also suitable are compounds such as 2-butene-1,4-

diol, as described in Feast, W.J., Harrison, B., J. Mol. Catal. **65**, 63 (1991), or 1-hexene (rearrangements).

The presence of an asymmetric centre in the compounds of formula II means that those compounds may occur in optically isomeric forms. Some compounds of formula II may occur in the form of tautomers (e.g. keto-enol tautomerism). If an aliphatic C=C double bond is present, then also geometric isomerism may occur (E-form or Z-form). In addition, exo/endo configurations are also possible. Formula II hence includes all possible stereoisomers, which are in the form of enantiomers, tautomers, diastereoisomers, E/Z isomers or mixtures thereof.

The alkyl, alkenyl and alkynyl groups in the definitions of the substituents may be straight-chain or branched. The same applies also to the alkyl moiety or each of the alkyl moieties of alkoxy, alkylthio, alkoxycarbonyl and other alkyl-containing groups. The alkyl groups contain preferably from 1 to 12, especially from 1 to 8, and more especially from 1 to 4, carbon atoms. The alkenyl and alkynyl groups contain preferably from 2 to 12, especially from 2 to 8, and more especially from 2 to 4, carbon atoms.

Alkyl includes, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl.

Hydroxyalkyl includes, for example, hydroxymethyl, hydroxyethyl, 1-hydroxyisopropyl, 1-hydroxy-n-propyl, 2-hydroxy-n-butyl, 1-hydroxyisobutyl, 1-hydroxy-sec-butyl, 1-hydroxy-tert-butyl and the various hydroxy-substituted isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl.

Haloalkyl includes, for example, fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2-fluoroethyl, 2-chloroethyl, 2,2,2-trichloroethyl and halogenated, especially fluorinated or chlorinated, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl and tert-butyl groups and the various halogenated isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl.

Alkenyl includes, for example, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Cycloalkyl is preferably C<sub>5</sub>-C<sub>8</sub>cycloalkyl, especially C<sub>5</sub>- or C<sub>6</sub>-cycloalkyl. Examples include cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Cyanoalkyl includes, for example, cyanomethyl (methylnitrile), cyanoethyl (ethylnitrile), 1-cyanoisopropyl, 1-cyano-n-propyl, 2-cyano-n-butyl, 1-cyanoisobutyl, 1-cyano-sec-butyl, 1-cyano-tert-butyl and the various isomers of cyanopentyl and cyanohexyl.

Aralkyl contains especially from 7 to 12 carbon atoms and more especially from 7 to 10 carbon atoms. It may be, for example, benzyl, phenethyl, 3-phenylpropyl,  $\alpha$ -methylbenzyl, 4-phenylbutyl or  $\alpha,\alpha$ -dimethylbenzyl.

Aryl contains preferably from 6 to 10 carbon atoms. It may be, for example, phenyl, pentalinyl, indenyl, naphthyl, azulinyl or anthryl.

Heteroaryl contains preferably 4 or 5 carbon atoms and one or two hetero atoms from the group oxygen, sulfur and nitrogen. It may be, for example, pyrrolyl, furanyl, thiophenyl, oxazolyl, thiazolyl, pyridyl, pyrazinyl, pyrimidinyl, pyridazinyl, indolyl, purinyl or quinolyl.

Heterocycloalkyl contains preferably 4 or 5 carbon atoms and one or two hetero atoms from the group oxygen, sulfur and nitrogen. It may be, for example, oxiranyl, azirinyl, 1,2-oxathiolanyl, pyrazolinyl, pyrrolidinyl, piperidyl, piperazinyl, morpholinyl, tetrahydrofuranyl or tetrahydrothiophenyl.

Alkoxy is, for example, methoxy, ethoxy, propyloxy, isopropyloxy, n-butyloxy, isobutyloxy, sec-butyloxy or tert-butyloxy.

Within the scope of the present invention, alkali metal is to be understood as meaning lithium, sodium, potassium, rubidium or caesium, especially lithium, sodium or potassium.

Within the scope of the present invention, alkaline earth metal is to be understood as meaning beryllium, magnesium, calcium, strontium or barium, especially magnesium or calcium.

In the above definitions, halogen is to be understood as meaning fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine.

Especially well-suited compounds of formula II in the composition according to the invention are those wherein  $Q_2$  is hydrogen.

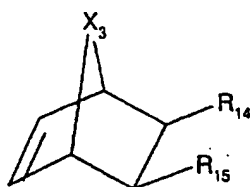
Preference is given also to compounds of formula II wherein  $Q_1$  is a radical having at least one carbon atom, which radical, together with the  $-CH=CQ_2-$  group, forms a 3- to 10-membered alicyclic ring that may contain a hetero atom selected from the group silicon, oxygen, nitrogen and sulfur and that is unsubstituted or substituted by halogen,  $-CN$ ,  $-NO_2$ ,  $R_1R_2R_3Si-$ ,  $-COOM$ ,  $-SO_3M$ ,  $-PO_3M$ ,  $-COO(M_1)_{1/2}$ ,  $-SO_3(M_1)_{1/2}$ ,  $-PO_3(M_1)_{1/2}$ ,  $C_1-C_6$ alkyl,  $C_1-C_6$ haloalkyl,  $C_1-C_6$ hydroxyalkyl,  $C_1-C_4$ cyanoalkyl,  $C_3-C_6$ cycloalkyl, phenyl, benzyl or by  $R_4-X$ ; or in which there may be fused to adjacent carbon atoms an aromatic or heteroaromatic or alicyclic ring that is unsubstituted or substituted by halogen,  $-CN$ ,  $-NO_2$ ,  $R_6R_7R_8Si-$ ,  $-COOM$ ,  $-SO_3M$ ,  $-PO_3M$ ,  $-COO(M_1)_{1/2}$ ,  $-SO_3(M_1)_{1/2}$ ,  $-PO_3(M_1)_{1/2}$ ,  $C_1-C_6$ alkyl,  $C_1-C_6$ haloalkyl,  $C_1-C_6$ hydroxyalkyl,  $C_1-C_4$ cyanoalkyl,  $C_3-C_6$ cycloalkyl, phenyl, benzyl or by  $R_{13}-X_1$ ;  $R_1$ ,  $R_2$  and  $R_3$  are each independently of the others  $C_1-C_4$ alkyl,  $C_1-C_4$ perfluoroalkyl, phenyl or benzyl;  $M$  is an alkali metal and  $M_1$  is an alkaline earth metal;  $R_4$  and  $R_{13}$  are each independently of the other  $C_1-C_6$ alkyl,  $C_1-C_6$ haloalkyl,  $C_1-C_6$ hydroxyalkyl or  $C_3-C_6$ cycloalkyl;  $X$  and  $X_1$  are each independently of the other  $-O-$ ,  $-S-$ ,  $-CO-$ ,  $-SO-$  or  $-SO_2-$  and  $R_6$ ,  $R_7$  and  $R_8$  are each independently of the others  $C_1-C_4$ alkyl,  $C_1-C_4$ perfluoroalkyl, phenyl or benzyl.

Norbornene and norbornene derivatives, especially dicyclopentadiene and dicyclopentadiene derivatives, are especially preferred as component (a).

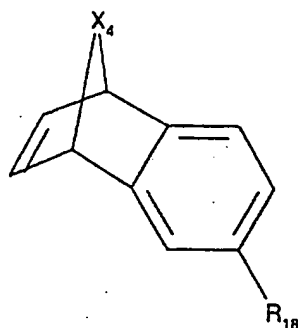
Preferred norbornene derivatives are the compounds of formulae III, IV, V and VI



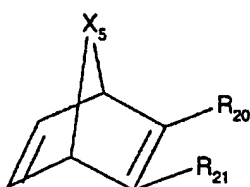
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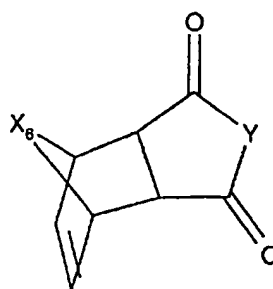
(III),



(IV),



(V),



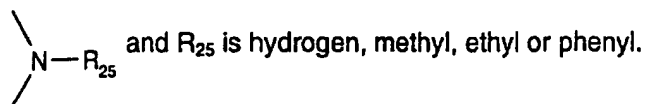
(VI),

wherein  $X_3$  is  $-\text{CHR}_{16}-$ , oxygen or sulfur,  $R_{14}$  and  $R_{15}$  are each independently of the other hydrogen,  $-\text{CN}$ , trifluoromethyl,  $(\text{CH}_3)_3\text{SiO}-$ ,  $(\text{CH}_3)_3\text{Si}-$  or  $-\text{COOR}_{17}$ , and  $R_{16}$  and  $R_{17}$  are each independently of the other hydrogen,  $\text{C}_1\text{-C}_{12}$ alkyl, phenyl or benzyl;

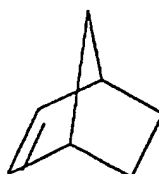
$X_4$  is  $-\text{CHR}_{18}-$ , oxygen or sulfur,  $R_{19}$  is hydrogen,  $\text{C}_1\text{-C}_{12}$ alkyl, phenyl or benzyl and  $R_{18}$  is hydrogen,  $\text{C}_1\text{-C}_6$ alkyl or halogen;

$X_5$  is  $-\text{CHR}_{22}-$ , oxygen or sulfur,  $R_{22}$  is hydrogen,  $\text{C}_1\text{-C}_{12}$ alkyl, phenyl or benzyl,  $R_{20}$  and  $R_{21}$  are each independently of the other hydrogen,  $\text{CN}$ , trifluoromethyl,  $(\text{CH}_3)_3\text{SiO}-$ ,  $(\text{CH}_3)_3\text{Si}-$  or  $-\text{COOR}_{23}$  and  $R_{23}$  is hydrogen,  $\text{C}_1\text{-C}_{12}$ alkyl, phenyl or benzyl;

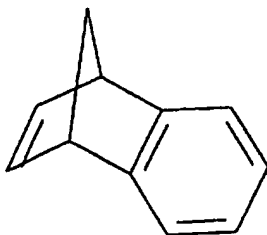
$X_6$  is  $-\text{CHR}_{24}-$ , oxygen or sulfur,  $R_{24}$  is hydrogen,  $\text{C}_1\text{-C}_{12}$ alkyl, phenyl or benzyl,  $Y$  is oxygen or



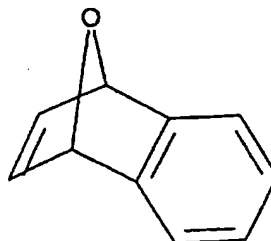
Examples of suitable compounds of formula II are the following cycloolefins:



(1),

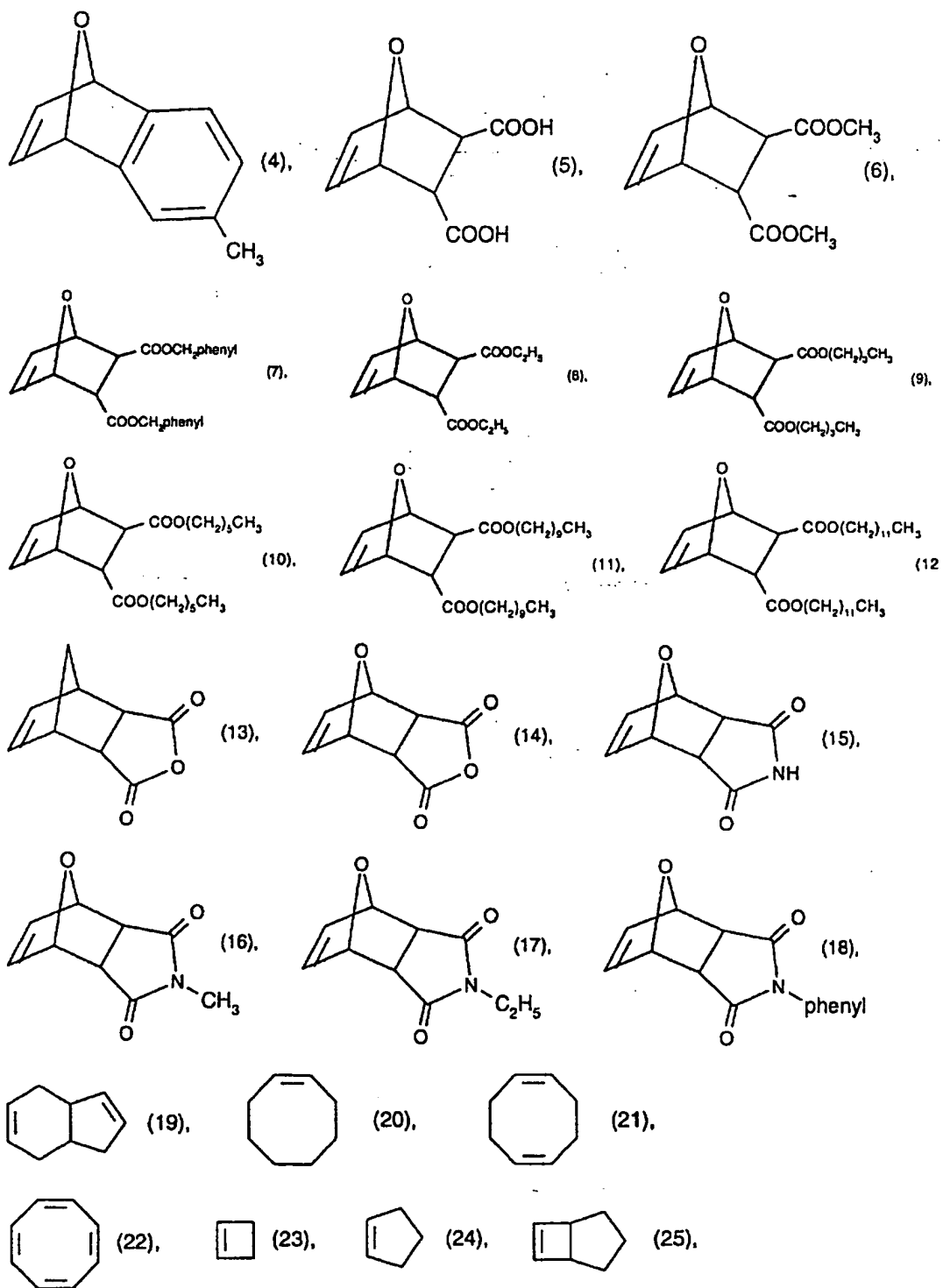


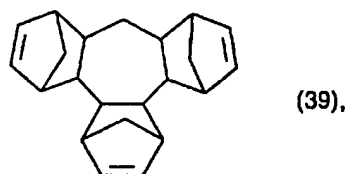
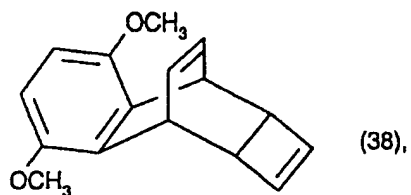
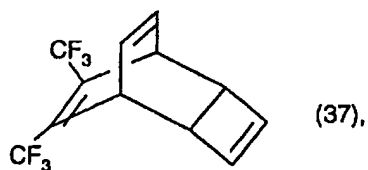
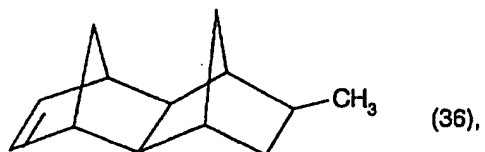
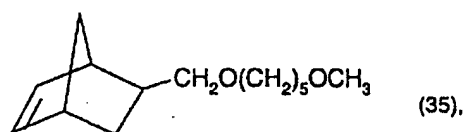
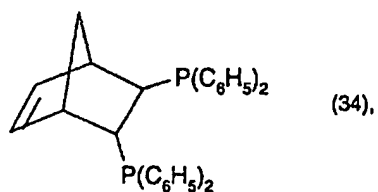
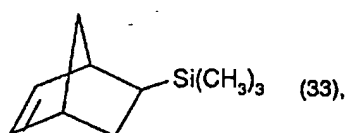
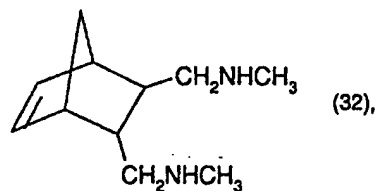
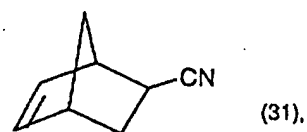
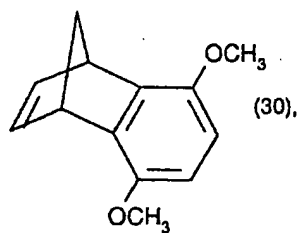
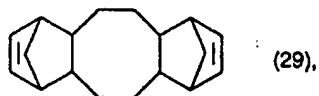
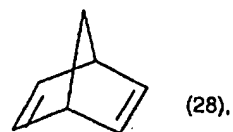
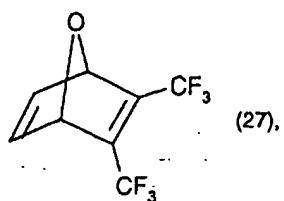
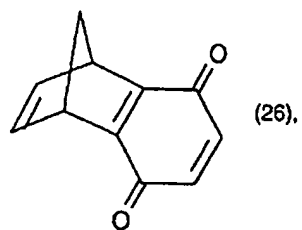
(2),



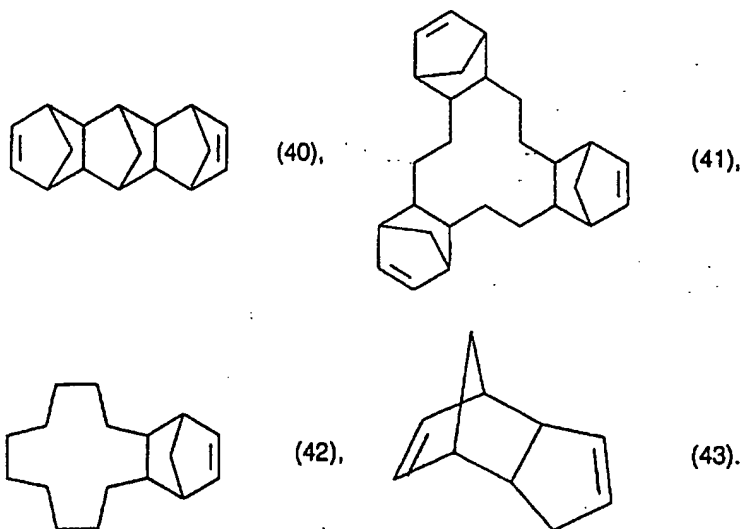
(3),

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In a preferred embodiment, the strained cycloolefins contain only carbon and hydrogen atoms, and are preferably 5- or 6-membered rings, or ring systems having from one to three 5- or 6-membered rings, for example norbornenes, alkylated norbornenes and dicyclopentadiene.

Especially preferred as component (a) is dicyclopentadiene.

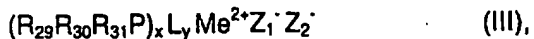
A large number of compounds of the transition metals titanium, vanadium, molybdenum, tungsten, rhenium, iridium, ruthenium and osmium are known to the person skilled in the art as catalysts for ring-opening metathesis polymerisation (ROMP catalysts). Such compounds are, for example, complex metal halides, metallo-carbenes or co-ordination catalysts of the Ziegler-Natta type. In principle, any of those known ROMP catalysts may be used as component (b) in the compositions according to the invention.

Preferably, a ruthenium(+II) complex salt or an osmium(+II) complex salt, especially a ruthenium(+II) complex salt, is used as component (b).

Since the fillers according to component (c) often contain small amounts of water, it is advisable to use ROMP catalysts that are not sensitive to moisture, such as, for example, the ruthenium(+II) and osmium(+II) complex salts described in WO 96/16100 and WO 96/20235.

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The preferred component (b) is therefore a complex salt of formula III



wherein  $R_{29}$ ,  $R_{30}$  and  $R_{31}$  are each independently of the others H,  $C_1$ - $C_{20}$ alkyl,  $C_1$ - $C_{20}$ alkoxy, unsubstituted or  $C_1$ - $C_6$ alkyl-,  $C_1$ - $C_6$ haloalkyl- or  $C_1$ - $C_6$ alkoxy-substituted  $C_4$ - $C_{12}$ cycloalkyl or cycloalkoxy, or unsubstituted or  $C_1$ - $C_6$ alkyl-,  $C_1$ - $C_6$ haloalkyl- or  $C_1$ - $C_6$ alkoxy-substituted  $C_6$ - $C_{16}$ aryl or  $C_6$ - $C_{16}$ aryloxy, or unsubstituted or  $C_1$ - $C_6$ alkyl-,  $C_1$ - $C_6$ haloalkyl- or  $C_1$ - $C_6$ alkoxy-substituted  $C_7$ - $C_{16}$ aralkyl or  $C_7$ - $C_{16}$ aralkyloxy; the radicals  $R_{30}$  and  $R_{31}$  together are unsubstituted or  $C_1$ - $C_6$ alkyl-,  $C_1$ - $C_6$ haloalkyl- or  $C_1$ - $C_6$ alkoxy-substituted tetra- or penta-methylene or tetra- or penta-methylenedioxy; or are tetra- or penta-methylene or tetra- or penta-methylenedioxy that is unsubstituted or substituted by  $C_1$ - $C_6$ alkyl,  $C_1$ - $C_6$ haloalkyl or  $C_1$ - $C_6$ alkoxy and fused with one or two 1,2-phenylene radicals; or are tetramethylenedioxy that is unsubstituted or substituted by  $C_1$ - $C_6$ alkyl,  $C_1$ - $C_6$ haloalkyl or  $C_1$ - $C_6$ alkoxy and fused in the 1,2- and 3,4-positions with 1,2-phenylene; and  $R_{31}$  is as defined hereinbefore; L is a neutral ligand, Me is Ru or Os,  $Z_1^-$  and  $Z_2^-$  are each a singly charged anion or  $Z_1^-$  and  $Z_2^-$  together are a doubly charged anion, x is a number from 1 to 3 and y is a number from 0 to 3, such that  $2 \leq x+y \leq 4$ .

The ligands L in the compounds of formula III may be identical or different.

The ruthenium and osmium compounds of formula III are known or can be prepared according to known processes from the metal halides (for example  $MeX_3$  or  $[Me\text{-arene}X_2]_2$ ) by reaction with phosphines of formula IV



wherein  $R_{29}$ ,  $R_{30}$  and  $R_{31}$  are as defined for formula (III), and ligand formers.

The radicals  $R_{29}$ ,  $R_{30}$  and  $R_{31}$  are preferably identical radicals. Also, sterically bulky radicals are preferred, for example branched, especially  $\alpha$ -branched, alkyl or alkoxy, or cyclic radicals.

$R_{29}$ ,  $R_{30}$  and  $R_{31}$  as alkyl may be linear or branched and contain preferably from 1 to 12, especially from 1 to 8, and more especially from 1 to 6, carbon atoms. Examples of alkyl are methyl, ethyl, n- and iso-propyl, n-, iso- and tert-butyl, and the isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl,

heptadecyl, octadecyl and eicosyl. Preferred examples are methyl, ethyl, n- and iso-propyl, n-, iso- and tert-butyl, 1-, 2- or 3-pentyl and 1-, 2-, 3- or 4-hexyl.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as alkoxy may be linear or branched and contain preferably from 1 to 12, especially from 1 to 8, and more especially from 1 to 6, carbon atoms. Examples of alkoxy are methoxy, ethoxy, n- and iso-propyloxy, n-, iso- and tert-butyloxy, and the isomers of pentyloxy, hexyloxy, heptyloxy, octyloxy, nonyloxy, decyloxy, undecyloxy, dodecyloxy, tridecyloxy, tetradecyloxy, pentadecyloxy, hexadecyloxy, heptadecyloxy, octadecyloxy and eicosyloxy. Preferred examples are methoxy, ethoxy, n- and iso-propyloxy, n-, iso- and tert-butyloxy, 1-, 2- or 3-pentyloxy and 1-, 2-, 3- or 4-hexyloxy.

Where R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> are substituted, the substituents are preferably C<sub>1</sub>-C<sub>4</sub>alkyl, C<sub>1</sub>-C<sub>4</sub>-haloalkyl or C<sub>1</sub>-C<sub>4</sub>alkoxy. Halogen is preferably chlorine and especially fluorine. Examples of preferred substituents are methyl, methoxy, ethyl, ethoxy and trifluoromethyl. R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> are preferably substituted by from 1 to 3 substituents.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as cycloalkyl are preferably C<sub>5</sub>-C<sub>8</sub>cycloalkyl and especially C<sub>5</sub>- or C<sub>6</sub>-cycloalkyl. Examples include cyclobutyl, cycloheptyl and cyclooctyl, and especially cyclopentyl and cyclohexyl. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-cyclopentyl and -cyclohexyl.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as cycloalkyloxy are preferably C<sub>5</sub>-C<sub>8</sub>cycloalkyloxy and especially C<sub>5</sub>- or C<sub>6</sub>-cycloalkyloxy. Examples include cyclobutyloxy, cycloheptyloxy and cyclooctyloxy, and especially cyclopentyloxy and cyclohexyloxy. Examples of substituted cycloalkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-cyclopentyloxy and -cyclohexyloxy.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as aryl are preferably C<sub>6</sub>-C<sub>12</sub>aryl and especially phenyl or naphthyl. Examples of substituted aryl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-phenyl.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as aryloxy are preferably C<sub>6</sub>-C<sub>12</sub>aryloxy and especially unsubstituted or substituted phenyloxy or naphthyloxy. Examples of substituted aryloxy are methyl-, dimethyl-, trimethyl-, methylisopropyl-, isopropyl-, diisopropyl-, triisopropyl-, tert-butyl-, methyltert-butyl-,

di(tert-butyl)-, tri(tert-butyl)-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-phenyloxy.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as aralkyl are preferably C<sub>7</sub>-C<sub>13</sub>aralkyl, the alkylene group in the aralkyl preferably being methylene. The aralkyl is especially benzyl. Examples of substituted aralkyl are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-benzyl.

R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> as aralkyloxy are preferably unsubstituted or substituted C<sub>7</sub>-C<sub>13</sub>aralkyloxy, the alkylene group in the aralkyloxy preferably being methylene. The aralkyloxy is especially unsubstituted or substituted benzyloxy. Examples of substituted aralkyloxy are methyl-, dimethyl-, trimethyl-, methoxy-, dimethoxy-, trimethoxy-, trifluoromethyl-, bis(trifluoromethyl)- and tris(trifluoromethyl)-benzyloxy.

Special preference is given to complex salts of formula III wherein R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> are C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>1</sub>-C<sub>6</sub>alkoxy, C<sub>4</sub>-C<sub>12</sub>cycloalkyl, C<sub>4</sub>-C<sub>12</sub>cycloalkoxy, C<sub>6</sub>-C<sub>16</sub>aryl or C<sub>6</sub>-C<sub>16</sub>aryloxy.

Especially preferred are complex salts of formula III wherein R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> are phenyl, tolyl or cyclohexyl.

Examples of suitable phosphines of formula IV are (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>P, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>3</sub>P, (C<sub>5</sub>H<sub>11</sub>)<sub>3</sub>P, (CH<sub>3</sub>)<sub>3</sub>P, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>P, (n-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>P, (iso-C<sub>3</sub>H<sub>7</sub>)<sub>3</sub>P, (n-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>P, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>HP, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)<sub>2</sub>HP, (C<sub>5</sub>H<sub>11</sub>)<sub>2</sub>HP, (CH<sub>3</sub>)<sub>2</sub>HP, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>HP, (n-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>HP, (iso-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>HP, (n-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>HP, (C<sub>6</sub>H<sub>5</sub>)H<sub>2</sub>P, (C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>)H<sub>2</sub>P, (C<sub>5</sub>H<sub>11</sub>)H<sub>2</sub>P, (CH<sub>3</sub>)H<sub>2</sub>P, (C<sub>2</sub>H<sub>5</sub>)H<sub>2</sub>P, (n-C<sub>3</sub>H<sub>7</sub>)H<sub>2</sub>P, (iso-C<sub>3</sub>H<sub>7</sub>)H<sub>2</sub>P, (n-C<sub>4</sub>H<sub>9</sub>)H<sub>2</sub>P, PH<sub>3</sub>, (2-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-CH<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2,4-di-CH<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (2,6-di-CH<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (2-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-C<sub>2</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-n-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-n-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-n-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-iso-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-iso-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-iso-C<sub>3</sub>H<sub>7</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-n-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-n-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-n-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-iso-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-iso-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-iso-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (3-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (4-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>P, (2-CH<sub>3</sub>-6-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (3-CH<sub>3</sub>-6-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (3-CH<sub>3</sub>-6-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (2,6-di-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P, (2,3-di-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P and (2,4-di-tert-C<sub>4</sub>H<sub>9</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>P.

Especially preferred phosphines are triisopropylphosphine, tri-tert-butylphosphine and tricyclohexylphosphine.

The ligands L bonded to the metal atom in the compounds of formula III may be photolabile or non-photolabile ligands.

In the case of compounds of formula III having photolabile ligands the catalytic activity is achieved by the action of light, that is to say on irradiation of the catalyst with light in the visible or ultraviolet range the photolabile ligand is removed, and a species is formed which is catalytically active for the metathesis polymerisation.

The photolabile ligands may be, for example, nitrogen ( $N_2$ ), unsubstituted or OH-,  $C_1$ - $C_4$ alkyl-,  $C_1$ - $C_4$ alkoxy-,  $C_6$ - $C_{12}$ aryl- or halo-substituted monocyclic, polycyclic or fused arenes having from 6 to 24, especially from 6 to 18, and more especially from 6 to 12, carbon atoms, or unsubstituted or  $C_1$ - $C_4$ alkyl-,  $C_1$ - $C_4$ alkoxy- or halo-substituted monocyclic heteroarenes, fused heteroarenes or fused arene-heteroarenes having from 3 to 22, especially from 4 to 16, and more especially from 4 to 10, carbon atoms and from 1 to 3 hetero atoms selected from the group oxygen, sulfur and nitrogen; or unsubstituted or  $C_1$ - $C_4$ alkyl-,  $C_1$ - $C_4$ alkoxy- or halo-substituted aliphatic, cycloaliphatic, aromatic or araliphatic nitriles having from 1 to 22, especially from 1 to 18, more especially from 1 to 12, and preferably from 1 to 7, carbon atoms. The preferred substituents are methyl, ethyl, methoxy, ethoxy, fluorine, chlorine and bromine. The arenes and heteroarenes are preferably substituted by from one to three radicals. The preferred heteroarenes are the electron-rich heteroarenes.

Examples of arenes and heteroarenes include benzene, biphenyl, naphthalene, anthracene, acenaphthene, fluorene, phenanthrene, pyrene, chrysene, fluoroanthrene, furan, thiophene, pyrrole, pyridine,  $\gamma$ -pyran,  $\gamma$ -thiopyran, pyrimidine, pyrazine, indole, cumarone, thionaphthene, carbazole, dibenzofuran, dibenzothiophene, pyrazole, imidazole, benzimidazole, oxazole, thiazole, isoxazole, isothiazole, quinoline, isoquinoline, acridine, chromene, phenazine, phenoxazine, phenothiazine, triazine, thianthrene and purine. Preferred arenes and heteroarenes are unsubstituted or substituted benzene, naphthalene, thiophene and benzthiophene. The arene is especially benzene unsubstituted or substituted by from one to three  $C_1$ - $C_4$ alkyl radicals and the heteroarene is preferably thiophene.

The nitriles may be substituted, for example, by methoxy, ethoxy, fluorine or chlorine; preferably, the nitriles are unsubstituted. The alkyl nitriles are preferably linear. Examples of



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nitriles include acetonitrile, propionitrile, butyronitrile, pentynitrile, hexynitrile, cyclopentyl- and cyclohexyl-nitrile, benzonitrile, methylbenzonitrile, benzylnitrile and naphthyl-nitrile. The nitriles are preferably linear C<sub>1</sub>-C<sub>4</sub>alkylnitriles or benzonitrile. Of the alkylnitriles, acetonitrile is especially preferred.

In a preferred sub-group, the photolabile ligands are N<sub>2</sub>, benzene unsubstituted or substituted by from one to three C<sub>1</sub>-C<sub>4</sub>alkyl radicals, thiophene, benzonitrile or acetonitrile.

Within the scope of the present invention "non-photolabile ligand" (also called "strongly coordinating ligand") denotes that the ligand does not dissociate, or dissociates only to an insignificant extent, from the catalyst on irradiation of the catalyst in the visible or near ultraviolet spectral range.

The non-photolabile ligands may be, for example, solvating inorganic and organic compounds containing the hetero atoms O, S or N, which are frequently also used as solvents. Examples of such compounds are H<sub>2</sub>O, H<sub>2</sub>S, NH<sub>3</sub>; unsubstituted or halogenated, especially fluorinated or chlorinated, aliphatic or cycloaliphatic alcohols or mercaptans having from 1 to 18, especially from 1 to 12, and more especially from 1 to 6, carbon atoms, aromatic alcohols or thiols having from 6 to 18, especially from 6 to 12, carbon atoms, araliphatic alcohols or thiols having from 7 to 18, especially from 7 to 12, carbon atoms; open-chained or cyclic and aliphatic, araliphatic or aromatic ethers, thioethers, sulfoxides, sulfones, ketones, aldehydes, carboxylic acid esters, lactones, carboxylic acid amides having from 2 to 20, especially from 2 to 12, and more especially from 2 to 6, carbon atoms which may be non-N-alkylated or N-C<sub>1</sub>-C<sub>4</sub>-mono- or -di-alkylated, and lactams which may be non-N-alkylated or N-C<sub>1</sub>-C<sub>4</sub>alkylated; and open-chained or cyclic and aliphatic, araliphatic or aromatic, primary, secondary and tertiary amines having from 1 to 20, especially from 1 to 12, and more especially from 1 to 6, carbon atoms.

Examples of such non-photolabile ligands are methanol, ethanol, n- and iso-propanol, n-, iso- and tert-butanol, 1,1,1-trifluoroethanol, bistrifluoromethylmethanol, tristrifluoromethylmethanol, pentanol, hexanol, methyl- or ethyl-mercaptan, cyclopentanol, cyclohexanol, cyclohexylmercaptan, phenol, methylphenol, fluorophenol, phenylmercaptan, benzylmercaptan, benzyl alcohol, diethyl ether, dimethyl ether, diisopropyl ether, di-n- or di-tert-butyl ether, tetrahydrofuran, tetrahydropyran, dioxane, diethyl thioether, tetrahydrothiophene, dimethyl sulfoxide, diethyl sulfoxide, tetra- and penta-methylene sulfoxide, dimethylsulfone,

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diethylsulfone, tetra- and penta-methylenesulfone, acetone, methyl ethyl ketone, diethyl ketone, phenyl methyl ketone, methyl isobutyl ketone, benzyl methyl ketone, acetaldehyde, propionaldehyde, trifluoroacetaldehyde, benzaldehyde, ethyl acetate, butyrolactone, dimethylformamide, dimethylacetamide, pyrrolidone and N-methylpyrrolidone.

The primary amines may correspond to the formula  $R_{26}NH_2$ , the secondary amines to the formula  $R_{26}R_{27}NH$  and the tertiary amines to the formula  $R_{26}R_{27}R_{28}N$ , wherein  $R_{26}$  is  $C_1$ - $C_{18}$ alkyl, unsubstituted or  $C_1$ - $C_4$ alkyl- or  $C_1$ - $C_4$ alkoxy-substituted  $C_5$ - or  $C_6$ -cycloalkyl, or unsubstituted or  $C_1$ - $C_4$ alkyl- or  $C_1$ - $C_4$ alkoxy-substituted  $C_6$ - $C_{18}$ aryl or  $C_7$ - $C_{12}$ aralkyl,  $R_{27}$  independently has the meaning given for  $R_{26}$ , or  $R_{26}$  and  $R_{27}$  together are tetramethylene, pentamethylene, 3-oxa-1,5-pentylene or  $-CH_2-CH_2-NH-CH_2-CH_2-$  or  $-CH_2-CH_2-N(C_1-C_4alkyl)-CH_2-CH_2-$ , and  $R_{28}$  independently has the meaning given for  $R_{26}$ . The alkyl contains especially from 1 to 12, and more especially from 1 to 6, carbon atoms. The aryl contains preferably from 6 to 12 carbon atoms and the aralkyl contains preferably from 7 to 9 carbon atoms. Examples of amines are methyl-, dimethyl-, trimethyl-, ethyl-, diethyl-, triethyl-, methylethyl-, dimethylethyl-, n-propyl-, di-n-propyl-, tri-n-butyl-, cyclohexyl-, phenyl- and benzyl-amine, and also pyrrolidine, N-methylpyrrolidine, piperidine, piperazine, morpholine and N-methylmorpholine.

Preferably, the compositions according to the invention comprise as component (b) a complex salt of formula III wherein L is an arene, a heteroarene, a nitrile, nitrogen ( $N_2$ ), an alcohol, an amine, CO,  $H_2O$  or  $NH_3$ .

Especially preferred as component (b) is a complex salt of formula III wherein L is benzene unsubstituted or substituted by from one to three  $C_1$ - $C_4$ alkyl radicals, thiophene, benzonitrile, acetonitrile, nitrogen ( $N_2$ ), an unsubstituted or partially or fully fluorinated  $C_1$ - $C_4$ alcohol, CO,  $H_2O$  or  $NH_3$ .

In the compounds of formula III,  $Z_1^-$  and  $Z_2^-$  may each be a singly charged anion, it being possible for  $Z_1^-$  and  $Z_2^-$  to be identical or different, or  $Z_1^-$  and  $Z_2^-$  may together be a doubly charged anion.

Suitable anions are, for example, hydride ( $H^-$ ), halide (for example  $Cl^-$ ,  $Br^-$  and  $I^-$ ),  $BF_4^-$ ,  $PF_6^-$ ,  $SbF_6^-$ ,  $AsF_6^-$ , unsubstituted or  $C_1$ - $C_4$ alkyl-,  $C_1$ - $C_4$ alkoxy-,  $(C_1-C_4alkyl)_3Si^-$  or  $(C_1-C_4alkyl)_3SiO^-$  substituted cyclopentadienyl-, or indenyl-, and the anions of oxyacids.

Further suitable anions are  $C_1-C_{12}^-$ , especially  $C_1-C_6^-$  and more especially  $C_1-C_4$ -alcoholates, which are especially branched and correspond, for example, to the formula  $R_xR_yR_zC-O^-$ , wherein  $R_x$  is H or  $C_1-C_{10}$ alkyl,  $R_y$  is  $C_1-C_{10}$ alkyl and  $R_z$  is  $C_1-C_{10}$ alkyl or phenyl. Examples are especially isopropoxy and tert-butoxy.

Other suitable anions are  $C_3-C_{18}^-$ , especially  $C_5-C_{14}^-$  and more especially  $C_5-C_{12}$ -acetylides, which may correspond to the formula  $R_w-C\equiv C^-$ , wherein  $R_w$  is  $C_1-C_{16}$ alkyl, preferably  $\alpha$ -branched  $C_3-C_{12}$ alkyl, for example of the formula  $R_xR_yR_zC-$ , or is phenyl or benzyl unsubstituted or substituted by from one to three  $C_1-C_4$ alkyl or  $C_1-C_4$ alkoxy radicals. Examples include isopropylacetylide, iso- and tert-butylacetylide, phenylacetylide, benzylacetylide, 2-methylphenylacetylide, 2-isopropylphenylacetylide, 2-isopropyl-6-methylphenylacetylide, 2-tert-butylphenylacetylide, 2,6-di-tert-butylphenylacetylide and 2-methyl-6-tert-butylphenylacetylide.

The anions of oxyacids may be, for example, sulfate, phosphate, perchlorate, perbromate, periodate, antimonate, arsenate, nitrate, carbonate, the anion of a  $C_1-C_8$ carboxylic acid, for example formate, acetate, propionate, butyrate, benzoate, phenylacetate, mono-, di- or tri-chloro- or -fluoro-acetate, sulfonates, for example methylsulfonate, ethylsulfonate, propylsulfonate, butylsulfonate, trifluoromethylsulfonate (triflate); phenylsulfonate or benzylsulfonate unsubstituted or substituted by  $C_1-C_4$ alkyl,  $C_1-C_4$ alkoxy or by halogen, especially fluorine, chlorine or bromine, for example tosylate, mesylate, brosylate, p-methoxy- or p-ethoxy-phenylsulfonate, pentafluorophenylsulfonate or 2,4,6-triisopropylsulfonate; and phosphonates, for example methylphosphonate, ethylphosphonate, propylphosphonate, butylphosphonate, phenylphosphonate, p-methylphenylphosphonate and benzylphosphonate.

Preferably,  $Z_1^-$  and  $Z_2^-$  in formula III are  $H^-$ ,  $Cl^-$ ,  $Br^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $SbF_6^-$ ,  $AsF_6^-$ ,  $CF_3SO_3^-$ ,  $C_6H_5-SO_3^-$ , p-toluenesulfonate (tosylate), 3,5-dimethylphenylsulfonate, 2,4,6-trimethylphenylsulfonate, 4-trifluoromethylphenylsulfonate or cyclopentadienyl.

Especially preferred ROMP catalysts of formula III are  $[(cyclohexyl)_3P]_2RuCl_2$ ,  $[(C_6H_5)_3P]_3RuCl_2$ ,  $[(C_6H_5)_3P]_3(CO)RuH_2$ ,  $[(C_6H_5)_3P]_3RuCl(cyclopentadienyl)$ ,

$[(\text{cyclohexyl})_3\text{P}]_2(\text{CH}_3\text{OH})\text{Ru}(\text{tosylate})_2$ ,  $[(\text{o-tolyl})_3\text{P}]_3\text{RuCl}_2$ ,  $[(\text{CH}_3)_2\text{CH}]_3\text{P}(\text{p-cymene})\text{RuCl}_2$  and especially  $(\text{cyclohexyl})_3\text{P}(\text{p-cymene})\text{RuCl}_2$ .

Suitable fillers which may be used as component (c) in the compositions according to the invention are, for example, metal powders, wood dust, glass powder, glass beads, semi-metal and metal oxides, for example  $\text{SiO}_2$  (Aerosils, quartz, quartz powder, vitreous fused silica), corundum and titanium oxide, semi-metal and metal nitrides, for example silicon nitride, boron nitride and aluminium nitride, semi-metal and metal carbides ( $\text{SiC}$ ), metal carbonates (dolomite, chalk,  $\text{CaCO}_3$ ), metal sulfates (barite, gypsum), and powdered rock and natural or synthetic minerals, mainly from the silicate series, for example talcum, mica, kaolin, wollastonite, bentonite and others.

Preferably, a metal oxide, carbonate, sulfate or silicate or  $\text{SiO}_2$  is used as component (c).

Preferred fillers are  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{CaCO}_3$ ,  $\text{CaSiO}_3$ ,  $\text{SiO}_2$ , woven glass fibres, woven carbon fibres and woven aramid fibres.

Especially preferred as component (c) are  $\text{Al}_2\text{O}_3$ ,  $\text{Al}(\text{OH})_3$ , wollastonite, quartz powder, dolomite, lime, chalk, woven glass fibres, woven carbon fibres and woven aramid fibres.

The silanes of formula I are known and can be prepared according to known methods. Some of those silanes are available commercially.

Preference is given to silanes of formula I wherein R as a monovalent organic group having from 2 to 100 carbon atoms is  $\text{C}_1\text{-C}_{20}$ alkyl,  $\text{C}_5\text{-C}_{20}$ aryl,  $\text{C}_6\text{-C}_{20}$ aralkyl,  $\text{C}_5\text{-C}_{12}$ cycloalkyl,  $\text{C}_2\text{-C}_{20}$ alkoxyalkyl,  $\text{C}_2\text{-C}_{20}$ alkenyl,  $\text{C}_4\text{-C}_{25}$ acryloxyalkyl,  $\text{C}_4\text{-C}_{25}$ methacryloxyalkyl,  $\text{C}_2\text{-C}_{20}$ aminoalkyl,  $\text{C}_4\text{-C}_{25}$ glycidylalkyl,  $\text{C}_7\text{-C}_{25}$ epoxycyclohexylalkyl or the radical of a polysiloxane.

Alkyl as R,  $\text{Y}_1$ ,  $\text{Y}_2$  or  $\text{Y}_3$  includes, for example, methyl, ethyl, isopropyl, n-propyl, n-butyl, isobutyl, sec-butyl, tert-butyl and the various isomers of pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl and eicosyl.

Aryl as R,  $\text{Y}_1$ ,  $\text{Y}_2$  or  $\text{Y}_3$  contains preferably from 6 to 10 carbon atoms. It may be, for example, phenyl, pentalinyl, indenyl, naphthyl, azulinyll or anthryl.

Aralkyl as R, Y<sub>1</sub>, Y<sub>2</sub> or Y<sub>3</sub> contains especially from 7 to 12 carbon atoms and more especially from 7 to 10 carbon atoms. It may be, for example, benzyl, phenethyl, 3-phenylpropyl,  $\alpha$ -methylbenzyl, 4-phenylbutyl or  $\alpha,\alpha$ -dimethylbenzyl.

Cycloalkyl as R, Y<sub>1</sub>, Y<sub>2</sub> or Y<sub>3</sub> is preferably C<sub>5</sub>-C<sub>8</sub>cycloalkyl, especially C<sub>5</sub>- or C<sub>6</sub>-cycloalkyl. Examples include cyclopropyl, dimethylcyclopropyl, cyclobutyl, cyclopentyl, methylcyclopentyl, cyclohexyl, cycloheptyl and cyclooctyl.

Examples of alkoxyalkyl as R, Y<sub>1</sub>, Y<sub>2</sub> or Y<sub>3</sub> are 2-methoxyethyl, 2-ethoxyethyl, 2-methoxypropyl, 3-methoxypropyl, 2-ethoxypropyl and 3-ethoxypropyl.

Alkenyl as R includes, for example, propenyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methylbut-2-enyl, n-oct-2-enyl, n-dodec-2-enyl, isododecenyl, n-octadec-2-enyl and n-octadec-4-enyl.

Examples of acryloxyalkyl and methacryloxyalkyl are 2-acryloxyethyl, 2-methacryloxyethyl, 3-acryloxypropyl and 3-methacryloxypropyl.

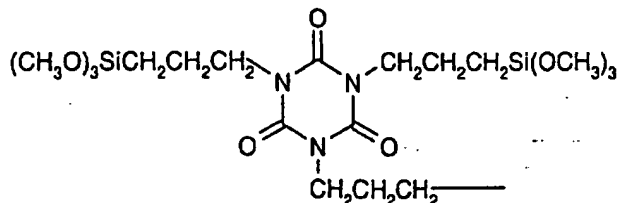
Suitable aminoalkyl groups are, for example, 2-aminoethyl, 3-aminopropyl, 3-aminobutyl and 4-aminobutyl.

Suitable glycidylalkoxyalkyl groups are, for example, 2-glycidylalkoxyethyl, 3-glycidylalkoxypropyl, 3-glycidylalkoxybutyl and 4-glycidylalkoxybutyl.

Epoxycyclohexylalkyl is preferably  $\beta$ -(3,4-epoxycyclohexyl)ethyl.

R in formula I is preferably methyl, ethyl, n-octyl, vinyl, 3-mercaptopropyl, 3-aminopropyl, 3-glycidylalkoxypropyl, 3-acryloxypropyl, 3-methacryloxypropyl,  $\beta$ -(3,4-epoxycyclohexyl)ethyl, N-( $\beta$ -aminoethyl)-3-aminopropyl, 3-ureidopropyl, 3-isocyanatopropyl, H<sub>2</sub>N-CH<sub>2</sub>CH<sub>2</sub>NH-CH<sub>2</sub>CH<sub>2</sub>NH-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-, (CH<sub>3</sub>O)<sub>3</sub>Si-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>- or a group of formula

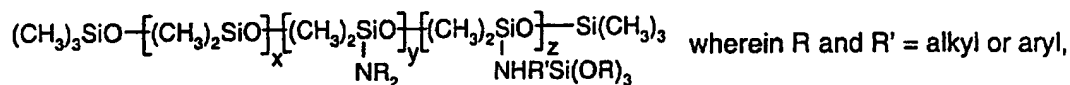
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Preference is given to silanes of formula I wherein R is methyl, vinyl, 3-mercaptopropyl or 3-aminopropyl.

$Y_1$ ,  $Y_2$  and  $Y_3$  in formula I are preferably methyl, ethyl, acetyl or 2-methoxyethyl.

Examples of suitable silanes of formula I are octyltriethoxysilane, methyltriethoxysilane, methyltrimethoxysilane, tris[3-(trimethoxysilyl)propyl]isocyanurate, vinyltriethoxysilane, vinyltrimethoxysilane, vinyl-tris(2-methoxyethoxy)silane,  $\gamma$ -methacryloxypropyltrimethoxysilane,  $\beta$ -(3,4-epoxycyclohexyl)ethyltrimethoxysilane,  $\gamma$ -glycidylloxypropyltrimethoxysilane,  $\gamma$ -mercaptopropyltrimethoxysilane,  $\gamma$ -aminopropyltriethoxysilane,  $\gamma$ -aminopropyltrimethoxysilane, N-( $\beta$ -aminoethyl)- $\gamma$ -aminopropyltrimethoxysilane,  $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2CH_2Si(OCH_3)_3$ , bis[ $\gamma$ -(trimethoxysilyl)propyl]amine, organically modified polydimethylsiloxane of formula



$\gamma$ -ureidopropyltrimethoxysilane,  $\gamma$ -isocyanatopropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-triethoxysilylpropylsuccinic acid anhydride, 3-methacryloxypropyltrimethoxysilane, vinyltris(2-methoxyethoxy)silane, vinyltriacetoxysilane, 3-mercaptopropyltrimethoxysilane, 3-glycidylloxypropyltriethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane and 3-(2-aminoethylamino)propylmethyldimethoxysilane.

Vinyltrimethoxysilane is especially preferred as component (d).

It should be mentioned that when using quartz powder as filler, it is also possible to use, instead of a mixture of components (c) and (d), a quartz powder pre-treated with a silane of formula I. Such quartz powders pre-treated with epoxysilane, alkylsilane or vinylsilane are

available commercially, for example under the names Silbond® W12 EST, Vp W12 VST and Vp W12 SST.

The amounts of components (a) to (d) in the compositions according to the invention may vary within wide limits.

Preferably, the compositions according to the invention contain from 15 to 75 % by weight of component (a), from 0.001 to 10.0 % by weight of component (b), from 20 to 80 % by weight of component (c) and from 0.01 to 20.0 % by weight of component (d), the sum of components (a), (b), (c) and (d) being 100 % by weight.

Especially preferred are compositions according to the invention containing from 25 to 65 % by weight, especially from 30 to 50 % by weight, of component (a), from 0.01 to 2.0 % by weight, especially from 0.1 to 1.0 % by weight, of component (b), from 30 to 75 % by weight, especially from 50 to 70 % by weight, of component (c) and from 0.05 to 10.0 % by weight, especially from 0.1 to 2.0 % by weight, of component (d).

The substance mixtures according to the invention can be prepared in customary manner by mixing the components using known mixing equipment (e.g. stirrers, rollers).

In addition to components (a) to (d), the composition according to the invention may comprise further customary additives, for example anti-oxidants, light stabilisers, plasticisers, colourants, pigments, thixotropic agents, viscosity improvers, anti-foams, antistatics, lubricants and mould release agents.

The composition according to the invention may be prepared directly before polymerisation, or may be used in the form of a preformulated mixture. Before polymerisation, the mixture can be stored in the form of a ready-to-use formulation for a prolonged period, which is advantageous for use on an industrial scale. Storage with the exclusion of light is recommended, however, when the catalyst contains photolabile ligands.

The present invention relates also to a method of bonding two or more substrates, which comprises applying a curable composition comprising the above-mentioned components (a) to (d) to at least one of the substrates to be bonded, bringing the substrates to be bonded

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into contact with one another, and curing the composition by heating to a temperature > 40°C.

Advantageously, the method according to the invention is carried out at a temperature of at least 60°C. The method according to the invention is especially carried out at temperatures of from 60 to 300°C, more especially from 60 to 250°C, preferably from 60 to 200°C and especially preferably from 70 to 160°C. After polymerisation, it may be advantageous to temper the mixture at elevated temperatures, for example at from 80 to 200°C.

The adhesive mixture is applied to the substrate in known manner. The layer thickness of the adhesive films is generally not more than 500 µm, and is preferably from 40 to 120 µm. It is, however, possible for substantially thicker layers to be fully cured thermally.

Before being coated with the adhesive mixture, the surfaces to be bonded may, if appropriate, be degreased and roughened.

After they have been brought together, the coated surfaces are pressed together or clamped, if appropriate.

Suitable surfaces for bonding are especially those made of metals, such as iron, steel, or especially aluminium and its alloys, for example with magnesium or silicon. The adhesive can also be used to bond two different materials, for example to bond metals to polymeric materials.

The bonds produced in accordance with the method according to the invention are distinguished especially by a high bond strength and minimal water absorption.

#### Example 1:

0.39 g of Norsorex NS (thermoplastic polynorbomene, Nippon Zeon) is dissolved at 80°C in 38.91 g of dicyclopentadiene. After cooling to 60°C, 0.5 g of vinyltrimethoxysilane (Silquest® A-171, Osi Specialties) and 0.2 g of (cyclohexyl)<sub>3</sub>P(p-cymene)RuCl<sub>2</sub> are added, and the mixture is stirred for 20 minutes at 60°C. After the addition, in portions, of 60 g of wollastonite FW 200 (Partek Minerals), the mixture is stirred for a further 15 minutes. The mixture is then degassed for from 3 to 5 minutes *in vacuo* (3 mbar).

The mixture so obtained is poured into a 4 mm-thick plate mould of aluminium and then fully cured (2 h/80°C, 4 h/100°C, 1 h/150°C). It is established that the cured moulding has very

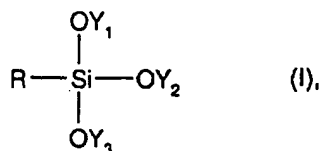


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good adhesion to aluminium and cannot be removed from the mould either at  $-180^{\circ}\text{C}$  or at  $200^{\circ}\text{C}$ .

**What is claimed is:**

1. Use, as an adhesive, of a composition comprising
  - (a) at least one strained cycloolefin,
  - (b) a catalyst for ring-opening metathesis polymerisation,
  - (c) a filler and
  - (d) a silane of formula I



wherein R is a monovalent organic group having from 2 to 100 carbon atoms, one or more of which may have been replaced by oxygen, sulfur, nitrogen or silicon atoms, and Y<sub>1</sub>, Y<sub>2</sub> and Y<sub>3</sub> are each independently of the others C<sub>1</sub>-C<sub>20</sub>alkyl, C<sub>5</sub>-C<sub>20</sub>aryl, C<sub>6</sub>-C<sub>20</sub>aralkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, C<sub>2</sub>-C<sub>20</sub>alkoxyalkyl or C<sub>1</sub>-C<sub>20</sub>acyl.

2. The use of a composition according to claim 1 as an adhesive for metals.
3. The use of a composition according to claim 1 as an adhesive for aluminium.
4. The use of a composition according to claim 1 comprising dicyclopentadiene as component (a).
5. The use of a composition according to claim 1 comprising (cyclohexyl)<sub>3</sub>P(p-cymene)RuCl<sub>2</sub> as component (b).
6. The use of a composition according to claim 1 comprising as component (c) Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, CaCO<sub>3</sub>, CaSiO<sub>3</sub>, SiO<sub>2</sub>, woven glass fibres, woven carbon fibres or woven aramid fibres.
7. The use of a composition according to claim 1 comprising as component (c) Al<sub>2</sub>O<sub>3</sub>, Al(OH)<sub>3</sub>, wollastonite, quartz powder, dolomite, lime, chalk, woven glass fibres, woven carbon fibres or woven aramid fibres.

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8. The use of a composition according to claim 1 comprising vinyltrimethoxysilane as component (d).

9. A method of bonding two or more substrates, which comprises applying a curable composition comprising components (a) to (d) according to claim 1 to at least one of the substrates to be bonded, bringing the substrates to be bonded into contact with one another, and curing the composition by heating to a temperature  $> 40^{\circ}\text{C}$ .

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